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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process to Recycle Aluminum Salt Cake Waste and to
Convert Aluminum Oxide to Hydrated Aluminum

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(73) Same as inventor

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Notice: This application is as filed and may therefore contain an
incomplete specification.

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ABSTRACT OF THE DISCLOSURE

A system process for treating aluminum salt cake containing water soluble halide salts and aluminum. The salt cake is contacted in a treatment tank with water having a temperature not less than about 250°C for a time sufficient to dissolve halide salts to form a saturated brine solution and to hydrate aluminum oxide. The hydrated aluminum oxide may be separated from the saturated brine solution and aluminum oxides and thereafter mixed with caustic to form sodium aluminate which is separated for further treatment. The saturated brine solution is cooled to a temperature of less than about 20°C to precipitate halide salts, which are separated. The brine solution may be cooled again to about 0°C to precipitate additional salts. Then the brine is reheated to a temperature not less than about 250°C by passing the cooled brine solution in heat exchange relationship with heated saturated brine solution leaving the treatment tank. The heated brine solution is introduced into the treatment tank with aluminum salt cake previously in the treatment tank for a time sufficient to form a saturated brine solution at a temperature in the range of from about 250°C to about 375°C.

A PROCESS TO RECYCLE ALUMINUM SALT CAKE WASTE
AND TO CONVERT ALUMINUM OXIDE TO HYDRATED ALUMINUM
CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U.S. Department of Energy and The University of Chicago representing Argonne National Laboratory.

BACKGROUND OF THE INVENTION

Scrap-aluminum recycling starts with the melting of the scrap aluminum in open-hearth reverberatory furnaces. In order to decrease the interfacial tension of the dross/aluminum and allow the aluminum to coalesce for easier separation as well as to minimize the oxidation of the molten aluminum and to capture the aluminum oxide that forms during the melting process, a salt mixture called flux, is spread on top of the bed. Flux typically consists of about 62% by weight sodium chloride, 32% by weight potassium chloride and 6% by weight other materials, including cryolite (Na_3AlF_6). This layer also serves to trap impurities such as magnesium chloride, which also reports to the flux layer. After the melting process is completed, the top layer of dark-colored material, called dross, is removed for further processing to recover some of its aluminum content. The black dross typically consists of aluminum metal (10-20% by weight), salt-flux mixture (40-55% by weight), and aluminum oxide (20-50% by weight). One of two methods is used to process the black dross for the recovery of aluminum: (1) reprocessing of the black dross in a rotary furnace (along with low grade scrap) or (2) physically separating the aluminum from the black dross using hammer mills. When the aluminum content of the dross is such that it is not economical to recover, the dross is disposed of in landfills. Rotary furnace processing requires the addition of salt fluxes in even larger quantities than that required for reverberatory furnace processing.

Residue generated by the rotary furnaces is referred to as salt cake, and it contains about 3-5% by weight aluminum, 15-30% by weight aluminum oxide, 30-45% by weight

sodium chloride, 20-30% by weight potassium chloride and minor amounts of the chlorides of impurities such as magnesium chloride. The amount of black-dross and salt-cake residues generated from U.S. secondary aluminum-smelting plants in 1988 was approximately 229×10^3 tons. The quantities of scrap and salt cake that are being processed are increasing. Because the salts are readily leachable, the disposal of this material in landfills is becoming more costly and less acceptable. Therefore, alternatives to disposal in landfills are in demand.

PRIOR ART

In Europe, prototype salt-cake-recycling systems (less than 60×10^3 t¹/yr) have been undergoing field testing and limited operation for a few years. Most of these systems have been installed in Italy and in Germany, countries in which the disposal of salt cake in conventional landfills is not permitted. Two organizations are marketing their systems in the United States: (1) Engitec Impianti, S.p.A. of Italy, which is represented in the United States by Lake Engineering, Inc. and (2) Berzelius Umwelt-Service AG. (B.U.S.), which is represented in the United States by Horsehead Resource Development Co., Inc. These systems devised by both of these organizations employ essentially the same steps, crushing and screening for aluminum recovery, salt leaching, off-gas treatment and evaporation/crystallization for salt recovery.

In 1977, Engitec installed its first system in Italy, a system that is capable of recovering 21×10^3 t of salt per year. In 1988, this plant was renovated and retrofitted with an energy-efficient evaporator/crystallizer equipped with a mechanical vapor compressor. Engitec has also pilot tested a proprietary flash evaporator to be used with small recycling plants, as well as a preconcentration unit for large-capacity evaporator/crystallizer systems.

The B.U.S. (German) system was installed in Germany about four years ago, and it has been in operation since that time. It was designed to process 50×10^3 short tons of salt cake and 13×10^3 short tons of ball mill dust per year.

So far, this plant has processed over 240×10^3 short tons of salt cake and ball mill dust. B.U.S. is planning to have two more operating plants in Germany by the end of 1991 bringing the total installed capacity to over 260×10^3 short tons per year. The salt recovered from this process meets the specifications of the smelters. In the last four years, 130×10^3 short tons of salt have been recovered and reused successfully by eight secondary aluminum smelters. Horsehead Resource Development Co., B.U.S.'s U.S. market business partner, estimated the capital cost for a 100-t/day system to be about \$35,000,000.

The U.S. Bureau of Mines developed, in the late 1970's, a method to recover aluminum, aluminum oxide, and fluxing salts from dross and salt cake. In this method, dross or salt cake is leached with water at room temperature to produce a saturated brine slurry. The slurry is screened to yield an aluminum-rich fraction that can be returned to the rotary furnace. The remaining slurry is vacuum filtered, yielding a clear brine solution and an aluminum-oxide cake. Evaporation of the clear brine solution results in over 80% of the metallic aluminum and essentially all of the fluxing salts being recovered. This method does not employ crushing of the salt cake or the dross. With the exception of the lack of crushing, the process steps are essentially the same as those employed in the European technologies.

American Recovery Technology Systems (ARTS) has designed, built, and is currently operating its first dross and salt-cake recycling system in Cleveland, Ohio. The plant has a capacity of processing about 65×10^3 t/yr. The closed-loop system consists essentially of the same processes employed in the European technologies; crushing, leaching and evaporation/crystallization. The evaporation is carried out at temperature of about 238°-240°F.

Alcan International Limited and Plasma Energy Corporation are currently developing a dross processing technology that does not require salt. This process uses a specially designed rotary furnace heated by a plasma-arc gas

heater. Inside the plasma torch are two tubular electrodes placed end-to-end but separated by a small gap. During operation, a process gas, such as air or nitrogen, is injected into the small gap between the electrodes. This arc heats the incoming gas to temperatures in excess of 5,000°C. At this temperature, the gas is dissociated and partially ionized. The ionized gas (plasma) is ejected out of the torch and into the rotary furnace to heat the dross.

The pilot dross-plasma-treatment plant was installed in 1988. The plasma torch is rated at 1 MW, and the capacity of the rotary furnace is about 3 t/h. The 1-MW torch uses 1.5-3 m³ of gas per minute. It is designed to process industrial scale samples of dross, and blocks up to 1 t can be charged (as can very dusty dross). The rotary furnace is designed to be airtight, and during its operation, the inside pressure is always maintained positive to prevent outside air infiltration. To date, about 400 tons of dross representing a total of about 150 batches, have been processed. The dross was supplied from various primary and secondary-aluminum production plants in the United States, Canada and Europe. The aluminum content in these samples ranged from 10% by weight to 80% by weight. The typical electrical energy input into the system per metric ton of dross processed was estimated by Alcan to be about 844 k Wh for the nitrogen plasma and 475 kWh for the air plasma.

The plasma dross-treatment process is an innovative and potentially cost-effective approach for the recovery of aluminum from the drosses of the primary aluminum industry. The key advantage of this process is that it eliminates the salt-flux requirements in dross processing. As a result, it can generate salt-free by-products, if the dross charged into the furnace did not contain any salt, as is typically the case in some of the drosses of the primary aluminum industry. If the dross processed contains salt flux, as in black dross, the salt will remain in the vitrified residual waste, which may not be leachable.

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As discussed earlier, several commercial processes are being developed for the leaching of chlorides from aluminum salt cake using water. These methods rely on the evaporation of water to concentrate and recover the salts after they are leached. This process is energy-intensive; it requires a minimum of about 0.64 k Wh/kg water processed using a single-stage evaporator. Licon, Inc. in Pensacola, Florida, stated in its literature that similar solutions can be concentrated by using about 50-100 Btu/lb (0.032-0.065 kWh/kg) of water removed. Licon's method uses vapor compression to recycle the latent heat and operates at reduced pressures in the range of 20-26 in. of mercury. The corrosive nature of the salt cake and dross may require special construction materials, resulting in increased costs.

OBJECTS OF THE INVENTION

An important object of the invention is to provide a process and system for treating aluminum salt cake wherein a portion of the saturated brine solution formed therefrom is treated to precipitate salt in an energy efficient high temperature and high pressure process.

Another object of the invention is to provide a system and process for treating aluminum salt cake which converts aluminum oxides normally considered a waste product to the hydrates which can be processed to aluminum.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation,

and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a graph showing the solubility of sodium and potassium salts as a function of temperature;

FIG. 2 is a graph showing the solubility of KCl, NaCl and actual salt cake as a function of temperature;

FIG. 3 is a schematic diagram of the inventive process and system; and

FIG. 4 is a schematic diagram of the inventive aluminum oxide hydration process and system.

DETAILED DESCRIPTION OF THE INVENTION

Solubility of salts in water as a function of temperature is shown by the data in Fig. 1 and Fig. 2 which compares the solubility of the individual salts which predominate in aluminum salt cake with a 50/50 mixture of the two salts with the solubility of the actual salt mixture which was extracted from a salt waste stream. Combining Figs. 1 and 2 demonstrates that the solubility of the potassium chloride and sodium chloride substantially increases with increasing temperature. The result of this is that less water will be needed to extract the same amount of salt when operating at a high temperature and also that less water will have to be heated and cooled to recover the same amounts of salt. The net result is less energy consumed by the inventive process.

Figs. 1 and 2 suggest at 300°C the solubility of the salts is about double that at room temperature. Therefore, half the amount of water required at room temperature will be required at 300°C. Preferably, the process is operated in the temperature range of from about 250°C to about 400°C.

In addition, operating at higher temperatures and pressures will enable heat recovery from the extracted stream and will eliminate the need for boiling of the water in the separation step. These phenomena will result in additional energy savings. Elevated pressures are required to be used in the subject system in order to prevent the water from boiling since in the inventive system and

process, the water is to be maintained liquid during the dissolution of salts therein.

Referring now to Fig. 3, there is disclosed a system 10 which includes a treatment tank 11 having a heater 12 with heating elements 13 disposed within the tank 11. There is a water inlet line 14 and water and salt outlet line 15 through which saturated brine leaves the treatment tank 11. A filter 17 filters out small particles which are carried with saturated brine from the tank 11.

The saturated brine leaves the filter 17 through a line 18 and enters a cooling chamber 20 which is specifically a shell and tube heat exchanger with the brine being on the shell side and flows therethrough and in heat exchange contact with the cooler fluid, as will be hereinafter explained, to an expansion valve 21. The saturated brine which is cooler as it exits the heat exchanger 20 flows through the expansion valve 21 to atmospheric pressure and a temperature less than about 20°C such as about 18°C where it is transported via a line 22 to a settlement tank 25. The settlement tank 25 is provided with a gas outlet port 26 to vent the gases which come out of the saturated brine solution during the cooling thereof, which gases may be collected and transported for further processing. The settlement tank 25 is provided with an exit line 27 through which wet salt is removed from the tank 25. Saturated liquid exits the tank 25 through line 28.

The line 28 leads to a second shell and tube heat exchanger 30 in which the brine from the settlement tank 25 is on the shell side and a cooling liquid from a chiller 35 is on the tube side, the cooled brine solution exiting the heat exchanger 30 by line 31 for transfer to a solid/liquid separator which may be in the form of cyclone 36 having a salt exit 37 and a brine exit 38. A make-up water line 39 leads along with line 38 to a pump 40 which pumps the combination of the brine from the solid/liquid separator 36 and the make-up water 39 to the tube side of the heat exchanger 20. As can be seen, there is provided in the system 10 a closed loop continuous process and system for

heating water to an elevated temperature, 300°C being shown for purposes of illustration only, it being understood that higher temperatures require higher pressures to maintain the water liquid. Moreover, the water when it is heated will, as illustrated in Figs. 1 and 2, dissolve more salt than when the water is cooled and therefore, the salt in saturated heated water will precipitate as the water is cooled.

For a system run at 300°C, the data indicate that less than 140 btu's will be required per pound of salt recovered. If the process were conducted at room temperature and water separated using a triple effect evaporator, the energy required would be about 1000 btu per pound of salt recovered. Accordingly, it is seen that the above system 10 and process results in substantial energy savings.

As will be understood, as the water in the treatment tank 11 is heated under pressure to temperatures in the range of from about 250°C to about 400°C, the aluminum oxide which is present in an amount up to about 50% by weight of the black cross has an opportunity to hydrate. The amount of time that it takes for aluminum oxide to hydrate under these conditions is perhaps longer than the amount of time it takes for the salt to dissolve to form a saturated brine solution, but nevertheless, aluminum oxides hydrate under these conditions. An alkaline environment will enhance the hydration rate of aluminum oxide so that the brine solution should have a high pH. Aluminum oxide hydrate is a useful starting material for the well known Bayer process, but aluminum oxide is not useful. Therefore, there is an opportunity in the above-identified system and process to provide an added economic benefit by hydrating a portion of aluminum oxides present in the salt cake material. This can be done in one of several ways.

For instance, aluminum oxides are solid and remain solid even when they are hydrated so that as the liquid circulates through the system 10 previously discussed, the aluminum oxide should remain in the treatment tank 11 and

they become hydrated over a period of time. When there is sufficient conversion of aluminum oxides to the hydrated aluminum oxides they may be removed from the treatment tank and separated from the remainder of the silica and other solids to be used as raw materials for the bayer process.

The Bayer process dissolves hydrated aluminum oxides in sodium hydroxide to form sodium aluminate which thereafter is seeded with aluminum hydroxide crystals to precipitate crystalline aluminum hydroxide. This process enables a relatively useless waste material, aluminum oxide, to be converted to a useful raw material as feedstock in the Hall-Heroult electrolytical process for making aluminum metal. Whether the aluminum oxide is hydrated to the trihydrate known as gibbsite or to the monohydrate known as boehmite is irrelevant. Moreover, whether the treatment tank 11 used in the system is used as a combination treatment tank to provide saturated brine solution at elevated temperatures and pressures and to hydrate the aluminum oxide or whether the aluminum oxides are transferred to a second holding tank, see Fig. 4, and held at elevated temperature and pressure for longer periods of time is irrelevant. The provision of a high temperature and high pressure process lends itself to the combination of both the energy saving production of salts and the production of hydrated aluminum oxide.

Accordingly, it is seen that a system and process have been provided for treating salt cake to recover salt in which substantial energy savings are available and at the same time to produce hydrated aluminum oxide useful as a starting material for the electrolytical production of aluminum metal.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for treating aluminum salt cake containing water soluble halide salts and aluminum oxides, comprising contacting the salt cake with water having a temperature not less than about 250°C for a time sufficient to dissolve halide salts therein to form a saturated brine solution and to hydrate aluminum oxide, separating the hydrated aluminum oxide from the saturated brine solution, cooling the saturated brine solution to a temperature of less than about 20°C to precipitate halide salts, separating the halide salts from the cooled brine solution, and reheating the brine solution to a temperature not less than about 250°C and contacting the heated brine solution with aluminum salt cake for a time sufficient to form a saturated brine solution at the elevated temperature and to hydrate aluminum oxides present in the salt cake.

2. The process of claim 1, wherein the water temperature is not greater than about 400°C during contact with the salt cake.

3. The process of claim 1, wherein the water temperature is maintained in the range of from about 250°C to about 375°C during contact with the salt cake.

4. The process of claim 1, wherein the cooled brine is transported to a settlement tank for salt to precipitate, any gases evolving from the saturated brine solution being separated for further treatment.

5. The process of claim 1, wherein the saturated brine solution is cooled to a temperature of less than about 5°C to precipitate halide salts.

6. The process of claim 1, wherein the heated brine is cooled to a temperature of about 0°C to precipitate about 1/2 the amount of salt dissolved in the heated saturated brine.

7. A process for treating aluminum salt cake containing water soluble halide salts and aluminum oxides, comprising contacting the salt cake in a treatment tank with

5 water having a temperature in the range of from about 250°C
to about 375°C at a pressure and for a time sufficient to
dissolve the halide salts therein to form a saturated brine
solution, cooling the saturated brine solution to a
temperature of not greater than about 20°C to precipitate
halide salts, separating the halide salts from the cooled
10 brine solution, and reheating the cooled brine solution to a
temperature not less than about 250°C by passing the cooled
brine solution in heat exchange relationship with heated
saturated brine solution leaving the treatment tank and
contacting the heated brine solution with aluminum salt cake
15 in the treatment tank for a time sufficient to form a
saturated brine solution at a temperature in the range of
from about 250°C to about 400°C.

8. The process of claim 7, wherein the water in the
treatment tank is maintained at a temperature greater than
about 300°C and at a pressure of not less than 86
atmospheres.

9. The process of claim 7, wherein the hot brine
from the treatment tank is first passed in heat exchange
relationship with the cooled brine after salts have
precipitated therefrom to heat the cooled unsaturated brine
5 and to cool the hot brine from the treatment tank to a
temperature of less than 250°C.

10. The process of claim 7, wherein the saturated
brine at less than about 250°C is passed through an
expansion valve to cool the brine to a temperature of less
than about 20°C and to reduce the pressure to about 1
5 atmosphere and thereafter is transported to a settlement
tank where the halide salts precipitate to the bottom
thereof and are removed while the brine solution is further
cooled to a temperature of less than about 5°C to
precipitate additional halide salts.

11. The process of claim 10, wherein the brine
solution at a temperature of less than about 5°C is pumped
to a heat exchanger where it is passed in heat exchange
relationship with hot brine at a temperature in the range of
5 from about 250°C to about 375°C leaving the treatment tank.

12. A process for treating aluminum salt cake containing water soluble halide salts and aluminum oxides, comprising contacting the salt cake with water having a temperature not less than about 250°C for a time sufficient to dissolve halide salts therein to form a saturated brine solution and to hydrate aluminum oxide, separating the hydrated aluminum oxide from the saturated brine solution and aluminum oxides, contacting the hydrated aluminum oxide with caustic to form sodium aluminate and separating same for further treatment, cooling the saturated brine solution to a temperature of less than about 20°C to precipitate halide salts, separating the halide salts from the cooled brine solution, and reheating the cooled brine solution to a temperature not less than about 250°C by passing the cooled brine solution in heat exchange relationship with heated saturated brine solution leaving the treatment tank and contacting the heated brine solution with aluminum salt cake in the treatment tank for a time sufficient to form a saturated brine solution at a temperature in the range of from about 250°C to about 400°C.

13. The process of claim 12, wherein the water temperature is not greater than about 375°C during contact with the salt cake.

14. The process of claim 12, wherein the water temperature is maintained in the range of from about 250°C to about 375°C during contact with the salt cake.

15. The process of claim 12, wherein the cooled brine is transported to a settlement tank for salt to precipitate, any gases evolving from the saturated brine solution being separated for further treatment.

16. The process of claim 12, wherein the saturated brine solution is cooled to a temperature of less than about 5°C to precipitate halide salts.

17. The process of claim 12, wherein the heated brine is cooled to a temperature of about 0°C to precipitate about 1/2 the amount of salt dissolved in the heated saturated brine.

18. The process of claim 12, wherein the hot brine from the treatment tank is first passed in heat exchange relationship with the cooled brine after salts have precipitated therefrom to heat the cooled unsaturated brine and to cool the hot brine from the treatment tank to a temperature of less than 250°C.

19. The process of claim 12, wherein the saturated brine at less than about 250°C is passed through an expansion valve to cool the brine to a temperature of less than about 20°C and to reduce the pressure to about 1 atmosphere and thereafter is transported to a settlement tank where the halide salts precipitate to the bottom thereof and are removed while the brine solution is further cooled to a temperature of less than about 5°C to precipitate additional halide salts.

20. The process of claim 12, wherein the brine solution at a temperature of less than about 5°C is pumped to a heat exchanger where it is passed in heat exchange relationship with hot brine at a temperature in the range of from about 250°C to about 375°C leaving the treatment tank.

21. A system for treating aluminum salt cake containing water soluble halide salts and aluminum oxides, comprising a treatment tank and heater means for heating water and aluminum salt cake to a temperature not less than about 250°C for a time sufficient to dissolve halide salts therein to form a saturated brine solution and to hydrate aluminum oxide, means for separating the hydrated aluminum oxide from the saturated brine solution, heat transfer means for cooling the saturated brine solution to a temperature of less than about 20°C to precipitate halide salts, means for separating the halide salts from the cooled brine solution, and means for reheating the brine solution to a temperature not less than about 250°C and contacting the heated brine solution with aluminum salt cake for a time sufficient to form a saturated brine solution at the elevated temperature and to hydrate aluminum oxides present in the salt cake.

22. A system for treating aluminum salt cake containing water soluble halide salts and aluminum oxides,

- comprising a treatment tank and heater means for heating water and aluminum salt cake to a temperature not less than about 250°C for a time sufficient to dissolve halide salts therein to form a saturated brine solution and to hydrate aluminum oxide, means for separating the hydrated aluminum oxide from the saturated brine solution and aluminum oxides, means for contacting the hydrated aluminum oxide with caustic to form sodium aluminate and separating same for further treatment, heat transfer means for cooling the saturated brine solution to a temperature of less than about 20°C to precipitate halide salts, means for separating the halide salts from the cooled brine solution, and means for reheating the cooled brine solution to a temperature not less than about 250°C by passing the cooled brine solution in heat exchange relationship with heated saturated brine solution leaving the treatment tank and contacting the heated brine solution with aluminum salt cake in the treatment tank for a time sufficient to form a saturated brine solution at a temperature in the range of from about 250°C to about 375°C.

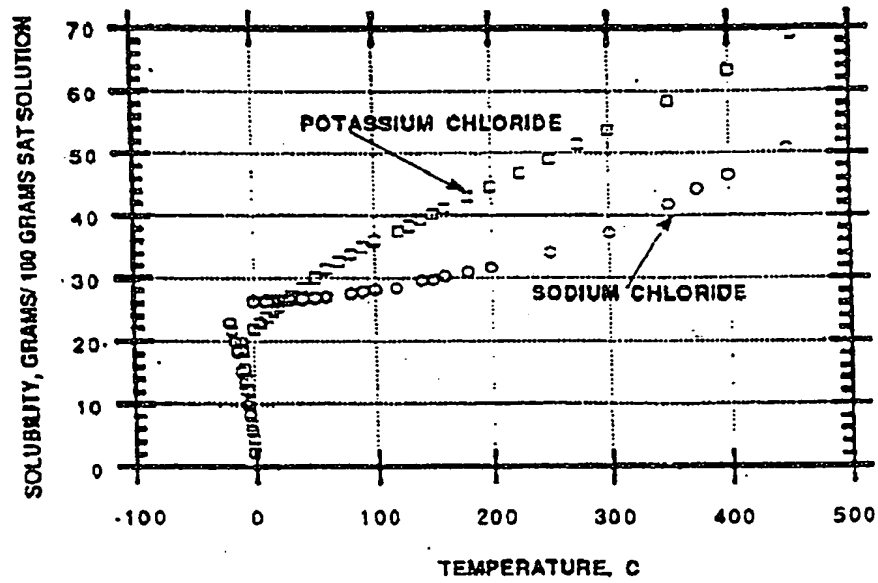


FIGURE 1

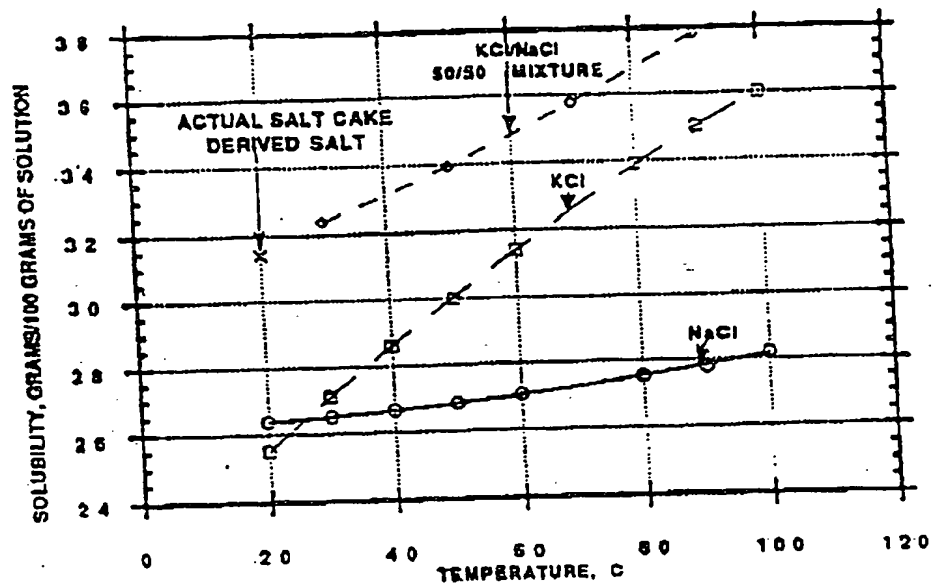


FIGURE 2

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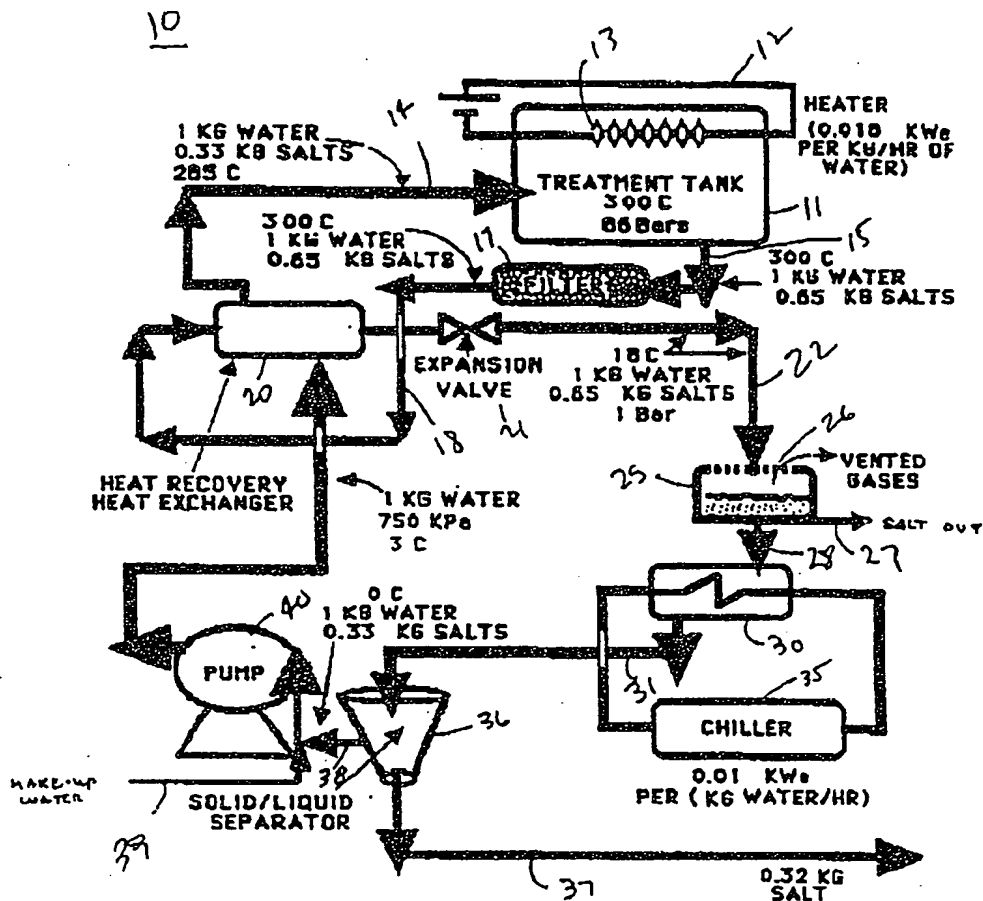


FIGURE 3

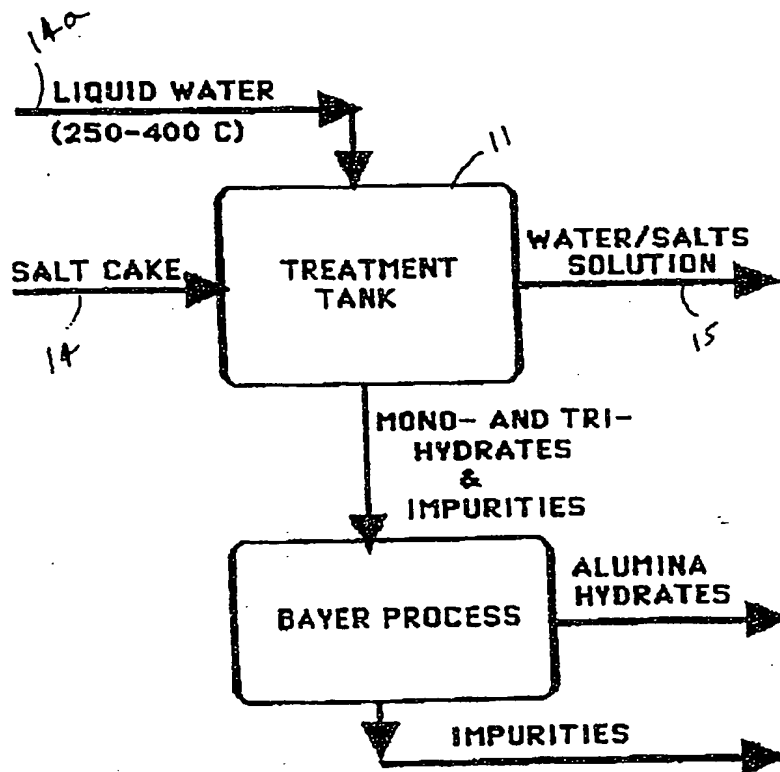


FIGURE 4